



# Cooperative hydrogen production and C–C coupling organic synthesis in one photoredox cycle

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## ABSTRACT

Coupling hydrogen fuel production with selective oxidative organic synthesis in one cooperative manner offers a promising avenue to enable efficient utilization of photoexcited carriers to achieve sustainable chemistry. Herein, a new Mo<sub>2</sub>N/Mn<sub>0.3</sub>Cd<sub>0.7</sub>S/CoPi photocatalyst is reported for visible-light-driven hydrogen production paired with selectively oxidative C–C bond formation. Mo<sub>2</sub>N acting as electron collectors and reduction sites are adsorbed on the Mn<sub>0.3</sub>Cd<sub>0.7</sub>S by interfacial Mo–S bond, while CoPi acting as hole collectors and active sites for oxidation reaction are deposited on Mo<sub>2</sub>N/Mn<sub>0.3</sub>Cd<sub>0.7</sub>S. Remarkably, the synergetic effect of Mo<sub>2</sub>N and CoPi dual cocatalysts results in the adjustable flexibility of switching benzaldehyde (BAD) production to C–C coupling synthesis, thus exhibiting the high selectivity of C–C coupling products. Mechanism studies indicate that the C–C coupling reaction occurs through a free radical mechanism. The present work gives insight for achieving highly efficient C–C coupling synthesis with hydrogen evolution by loading dual cocatalysts.

## 1. Introduction

Photocatalytic water splitting is considered as one of the promising pathways to convert solar energy for the production of clean and renewable chemical energy [1,2]. Most H<sub>2</sub> production studies have focused on the reduction reaction, but paid less attention to the oxidation half-reaction [3,4]. Coupling oxygen evolution with the hydrogen production is the ideal reaction. However, O<sub>2</sub> formation has rarely been reported because of the need for 4 h<sup>+</sup> per O<sub>2</sub> molecule and its difficult desorption. [5–8] To solve this issue, sacrificial reagents such as lactic acid (LA) are commonly employed to trap holes to improve the reaction efficiency, which however undesirably wastes the energy of holes, brings along useless oxidation products [9–11]. In this context, to construct a dual-functional photocatalytic reaction system pairing selective oxidative organic synthesis and H<sub>2</sub> production in a cooperative manner would enable sufficient utilization of photogenerated electrons and holes to meet the economic and social sustainability goal.

Biomass from raw materials to intermediates is the most renewable earth-abundant source, which can be used as ideal sacrificial reagents [12]. Exploiting biomass derivatives (such as alcohols, amines, and sugars) to consume holes, while leaving electrons for the proton reduction to H<sub>2</sub>, significantly contributes to affordable and renewable

energy production [13]. Benzyl alcohol (BA) is important platform compound that can be derived from various biomass resources. Oxidation of benzyl alcohol (BA) to either carbonyls or C–C coupled products and its derivatives is a route to produce useful value-added chemicals [14–16]. To date, most reports are primarily focused on the oxidation of BA to benzaldehyde (BAD). Recently, the progress of C–C synthesis from BA has been reported [17]. For example, the visible light-driven transformation of benzyl alcohol to C–C coupled products on zero-dimensional (0D) CdS quantum dots has been reported, however featuring a poor selectivity with mixture of hydrobenzoin, deoxybenzoin, and benzil [18]. The co-production of benzyl alcohol to its C–C coupling products (benzoin or deoxybenzoin) and hydrogen (H<sub>2</sub>) has been achieved on Zn<sub>x</sub>In<sub>2</sub>S<sub>3+x</sub>, [19] but still suffering from the low selectivity of each C–C coupling products. Notably, the C–C coupled products from BA, such as hydrobenzoin (HB) and benzoin (BZ), can be used as versatile structural motifs in fine chemicals and pharmaceutical intermediates that have a broad range of applications in chiral and synthetic chemistry [20,21].

In this work, we report Mn<sub>0.3</sub>Cd<sub>0.7</sub>S nanorods modified with synergistic dual cocatalysts CoPi and Mo<sub>2</sub>N bifunctional reaction system enabling efficient visible-light-driven H<sub>2</sub> production and simultaneous transformation of BA to value-added C–C coupled products in one redox

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cycle. The results demonstrate that the CoPi can be an oxidation active site to accumulate photo-generated holes, while the Mo<sub>2</sub>N can capture and transport the photo-generated electrons and provide the active site for H<sub>2</sub> production. Due to such synergetic effect of CoPi and Mo<sub>2</sub>N cocatalysts, the photo-induced carriers can be efficiently separated, leading to a higher performance for photocatalytic H<sub>2</sub> production and effectively tunes the product selectivity of BA oxidation. In addition, the in-situ electron paramagnetic resonance (EPR) spectroscopic measurements show that the C<sub>α</sub> radical is an important intermediate for BA oxidation, proving that the C–C coupling occurs through a free radical mechanism. It is hoped that this work could open a new horizon for designing novel heterogeneous photocatalysts based cooperative photoredox systems toward simultaneous use of photogenerated electrons and holes pairs for solar-to-chemical energy conversion to value-added fuels and organic chemicals.

## 2. Experimental section

### 2.1. Materials

Thioacetamide (CH<sub>3</sub>CSNH<sub>2</sub>), ethylenediamine (C<sub>2</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>), cadmium acetate dehydrate (Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O), sodium phosphate monobasic ((NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O), manganese acetate tetrahydrate (Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O), disodium hydrogen phosphate ((Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O), cobalt nitrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), molybdenum (> 99% purity), H<sub>2</sub>O<sub>2</sub> (> 30%), sodium sulfide nonahydrate (Na<sub>2</sub>S·9H<sub>2</sub>O), sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>) and chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, 37.5% Pt basis) were obtained from Sinopharm Chemical Reagent Co., Ltd.

### 2.2. Materials synthesis

#### 2.2.1. Synthesis of Mo<sub>2</sub>N nanoparticles (NPs)

Mo<sub>2</sub>N NPs were synthesized by calcining MoO<sub>3</sub> in NH<sub>3</sub> atmosphere. In detail, 1 g molybdenum powder was dissolved into 15 mL of H<sub>2</sub>O<sub>2</sub> (30%) under constant stirring. After stirring for 45 min, transferred to a Teflon-lined autoclave and maintained at 180 °C for 48 h. The samples were cooled down to ambient temperature, and the precipitate was separated by filtration by washing with DI water. The as-prepared molybdenum trioxide nanowires (MoO<sub>3</sub> NWs) were obtained after freeze-dried. The molybdenum nitride nanoparticles (Mo<sub>2</sub>N NPs) were obtained by calcining the MoO<sub>3</sub> samples in NH<sub>3</sub> for 6 h at 750 °C. The XPS result (Fig. S1) shows that passivation layer is formed on the surface of the synthesized sample, and the surface molybdenum is mixed with Mo<sup>6+</sup>, Mo<sup>4+</sup> and Mo<sup>3+</sup>, and the stoichiometric ratio of molybdenum to nitrogen in the samples determined by ICP-AES and elemental analysis is about 2:1 (Table S1).

#### 2.2.2. Synthesis of Mn<sub>0.3</sub>Cd<sub>0.7</sub>S nanorods (NRs)

The Mn<sub>0.3</sub>Cd<sub>0.7</sub>S NRs were prepared by a solvothermal method. Detailed preparation process was demonstrated in supporting information.

#### 2.2.3. Preparation of Mo<sub>2</sub>N/Mn<sub>0.3</sub>Cd<sub>0.7</sub>S (Mo/MCS) composites

A certain amount of the Mo<sub>2</sub>N (2 mg/mL) suspension was added to MCS aqueous suspension (2 mg/mL). The mixture was stirred vigorously for 2 h without light, washed with deionized water and dried at 80 °C to obtain aMo/MCS samples (a = 5, 7 and 10, the mass percentage of Mo<sub>2</sub>N to MCS).

#### 2.2.4. Preparation of Mo<sub>2</sub>N/Mn<sub>0.3</sub>Cd<sub>0.7</sub>S/CoPi (Mo/MCS/Co) composites

Cobalt phosphate cocatalyst was loaded on the Mo/MCS sample by photodeposition method. Typically, 40 mg 7Mo/MCS was dispersed in 50 mL 0.1 M phosphate buffer solution (pH = 7.0), a certain amount of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O is added, then the composite is obtained by centrifugation and washing after stirring for 2 h under irradiation, and denoted as 7Mo/MCS/bCo (b = 1, 2 and 3, the mass percentage of CoPi to MCS).

The blank CoPi and MCS/Co composite were prepared by the same procedure without adding 7Mo/MCS and replacing 7Mo/MCS with MCS.

### 2.3. Characterization

The instrument model used for characterization was demonstrated in the support information, which was reported in our previous works [9]. Detailed experimental process was demonstrated in supporting information.

### 2.4. Photocatalytic Testing

The photocatalytic hydrogen (H<sub>2</sub>) production integrated with hydrobenzoin (HB) synthesis was performed in a double-walled quartz reactor and the temperature of the solution was maintained at 25 °C by a flow of circulating water. Typically, 10 mg samples were added into 10 mL of CH<sub>3</sub>CN containing 50 μL (0.48 mmol) of BA. The reaction suspension was purged with Ar gas for 30 min. A 300 W Xe lamp (PLS-SXE 300D, Beijing Perfectlight Co., Ltd.) was used as the light source (λ ≥ 420 nm), and the light power density is 300 mW cm<sup>-2</sup> measured by a photoradiometer (PL-MW2000, Beijing Perfectlight Co., Ltd.). The evolved H<sub>2</sub> was quantified by a gas chromatograph (Shimadzu GC-8A 2014 C). The liquid products were analyzed by high-performance liquid chromatography (HPLC) analysis (Shimadzu HPLC-LC20AT), which also were monitored by gas chromatography–mass spectroscopy (Shimadzu GC–MS QP 2020, Q-Exactive).

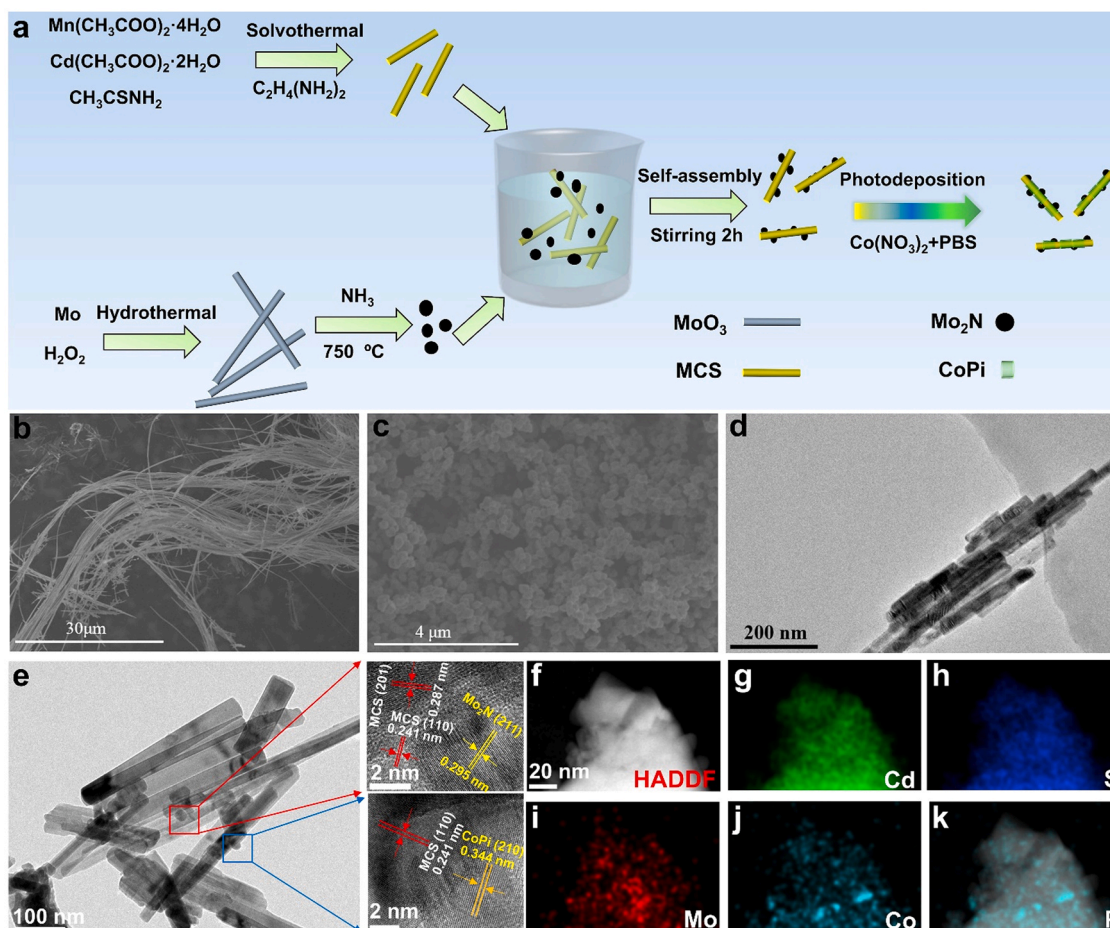
### 2.5. Charge Flow Tracking by Photo-deposition

Photo-deposition of 1.5 wt% Pt and PbO<sub>2</sub> on the surfaces of 7Mo/MCS/2Co was carried out using H<sub>2</sub>PtCl<sub>6</sub> and Pb(NO<sub>3</sub>)<sub>2</sub> as precursors, respectively, which was reported in our previous works [9].

## 3. Results and discussion

### 3.1. Morphology analysis

The overall fabrication procedure for Mo<sub>2</sub>N/Mn<sub>0.3</sub>Cd<sub>0.7</sub>S/CoPi (Mo/MCS/Co) composite is schematically pictured in Fig. 1a. The scanning electron microscopy (SEM) shows the obtained MoO<sub>3</sub> sample (Figs. S2a and 1b) is a 1D nanowires (NWs) structure, after the NH<sub>3</sub> reduction process, the obtained black sample is Mo<sub>2</sub>N nanoparticles (NPs) (Figs. S2b and 1c). Subsequently, the Mo<sub>2</sub>N/Mn<sub>0.3</sub>Cd<sub>0.7</sub>S (Mo/MCS) composites were prepared by electrostatic self-assembly method. The opposite charged surfaces of Mo<sub>2</sub>N and MCS (Fig. S3) result in them assemble into Mo/MCS composites driven by the forces of electrostatic attraction. Finally, the cobalt phosphate (CoPi) have been deposited on the Mo/MCS composites through a photodeposition method. Co<sup>2+</sup> ions can be oxidized into Co<sup>3+</sup> by photogenerated holes of MCS NRs and the Co<sup>3+</sup> has limited solubility at aqueous buffer solution with pH = 7, cobalt phosphate (CoPi) will deposit on the surface of Mo/MCS composites [22]. To check the microscopic morphology and structure information of the dual-cocatalysts composite, transmission electron microscopy (TEM) has been executed. As revealed in Fig. 1e, the 7Mo/MCS/2Co composite shows 1D nanorod morphology, with Mo<sub>2</sub>N or CoPi nanoparticles dispersed on its surface. The lattice fringes with a distance of 0.295 nm matches the (211) plane of Mo<sub>2</sub>N well. The pronounced lattice spacings of 0.287 and 0.241 nm correspond to the (201) and (110) plane of hexagonal phase MCS, respectively. The lattice fringes with a distance of 0.344 nm matches the (210) plane of CoPi. These results illustrate the successful combination of MCS and Mo<sub>2</sub>N/CoPi. In addition, energy-disperse X-ray mapping (EDX-mapping) (Fig. 1f–k) show that the Mo<sub>2</sub>N and CoPi nanoparticles dispersed on the surface of MCS.



**Fig. 1.** (a) Schematic diagram for the preparation of Mo/MCS/Co photocatalysts. FESEM images of (b)  $\text{MoO}_3$  and (c)  $\text{Mo}_2\text{N}$ . (d) TEM image of MCS, (e) HRTEM image and (f–k) EDX of the 7Mo/MCS/2Co.

### 3.2. Structural characteristics

The crystal structures of these synthetic samples have been employed by X-ray diffraction (XRD). As shown in Fig. 2a, the diffraction peaks located at  $24.9^\circ$ ,  $26.6^\circ$ ,  $28.5^\circ$ ,  $44.2^\circ$  and  $52.5^\circ$  correspond to (100), (002), (101), (110) and (112) crystallographic planes of hexagonal solid solution  $\text{Mn}_{0.3}\text{Cd}_{0.7}\text{S}$  [9]. The diffraction peaks of CoPi are in a good agreement with those of monoclinic  $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  (JCPDS NO. 33-0432) [23]. The diffraction peaks located at  $37.1^\circ$ ,  $42.9^\circ$ ,  $62.4^\circ$  and  $74.9^\circ$  are assigned to (111), (200), (220) and (311) crystallographic planes of cubic  $\text{Mo}_2\text{N}$  (JCPDF 25-1366), respectively. After loading of  $\text{Mo}_2\text{N}$  or/and CoPi on  $\text{Mn}_{0.3}\text{Cd}_{0.7}\text{S}$ , the XRD patterns have no obvious changes for 7Mo/MCS, MCS/2Co and 7Mo/MCS/2Co. No diffraction peaks of  $\text{Mo}_2\text{N}$  and CoPi are observed in these composites, and this phenomenon could be ascribed to the lower  $\text{Mo}_2\text{N}$  and CoPi content.

Fig. 2b shows the UV-Vis diffuse reflectance spectroscopy (DRS) of the as-obtained samples. The absorption band edge of CoPi sample locates at around 280 nm, and the optical absorption in the range of 400–700 nm corresponds to the d-d electron transition of Co (II) [24]. The bare  $\text{Mo}_2\text{N}$  presents a broad and intense absorption in the range of 250–800 nm, which is consistent with its black color [25]. The band gap of blank MCS is determined to be of 2.44 eV based on its UV-vis DRS with the Tauc plot (Fig. S4). Compared with the blank MCS NRs, a red shift of optical absorption was observed over all the 7Mo/MCS, MCS/2Co and 7Mo/MCS/2Co composites.  $\text{N}_2$  adsorption-desorption tests are conducted to gain information about surface properties of the sample. As listed in Table S2, it can be seen that compared with MCS NRs, the BET specific surface area of 7Mo/MCS, MCS/2Co and

7Mo/MCS/2Co increase from  $22.99 \text{ m}^2 \text{ g}^{-1}$  to 34.84, 33.17, and  $35.02 \text{ m}^2 \text{ g}^{-1}$ , respectively. The increased surface area may offer abundant exposed catalytic-active sites and improve the photocatalytic activity.

X-ray photoelectron spectrum (XPS) provides valuable chemical composition and binding states of elements on the surface of 7Mo/MCS/2Co composite. As compared with bare MCS NRs, the peaks in both Cd 3d region (411.2 and 404.4 eV) and Mn 2p region (651.8 and 640.8 eV) shifted towards higher binding energy (Fig. 2c, d). As shown in Fig. 2f, the peak at 226.7 eV verified the formation of Mo-S bond, and the existence of Mo-S bonds facilitates the transfer of photo-generated charges [26]. Compared with  $\text{Mo}_2\text{N}$ , the binding energy of Mo 3d and N 1 s of 7Mo/MCS/2Co are negatively shifted, suggesting the existence of interaction among  $\text{Mo}_2\text{N}$  and MCS in the composites (Fig. 2f, g) [27]. In the case of Co 2p XPS spectrum (Fig. 2h), the peaks of Co  $2p_{3/2}$  and Co  $2p_{1/2}$  are located at 781.87 eV, 797.99 eV, 785.52 eV and 801.97 eV (satellite peaks at 788.38 eV and 805.08 eV), which proves the composition of  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  [28]. The P 2p peak at 133.1 eV (Fig. 2i) is indicative of  $\text{PO}_4^{3-}$  in the CoPi phase [22].

### 3.3. Photocatalytic performance

The dehydrogenative C–C coupling of benzyl alcohol (BA) into hydrobenzoin (HB) and  $\text{H}_2$  performance was evaluated over the as-prepared samples under visible light. It was found that the production rates of  $\text{H}_2$  and HB are calculated to be ca. 1.0, suggesting a stoichiometric dehydrogenation reaction. Only relatively low activity for converting BA to benzaldehyde (BAD) appears on MCS (Fig. 3a). Notably,



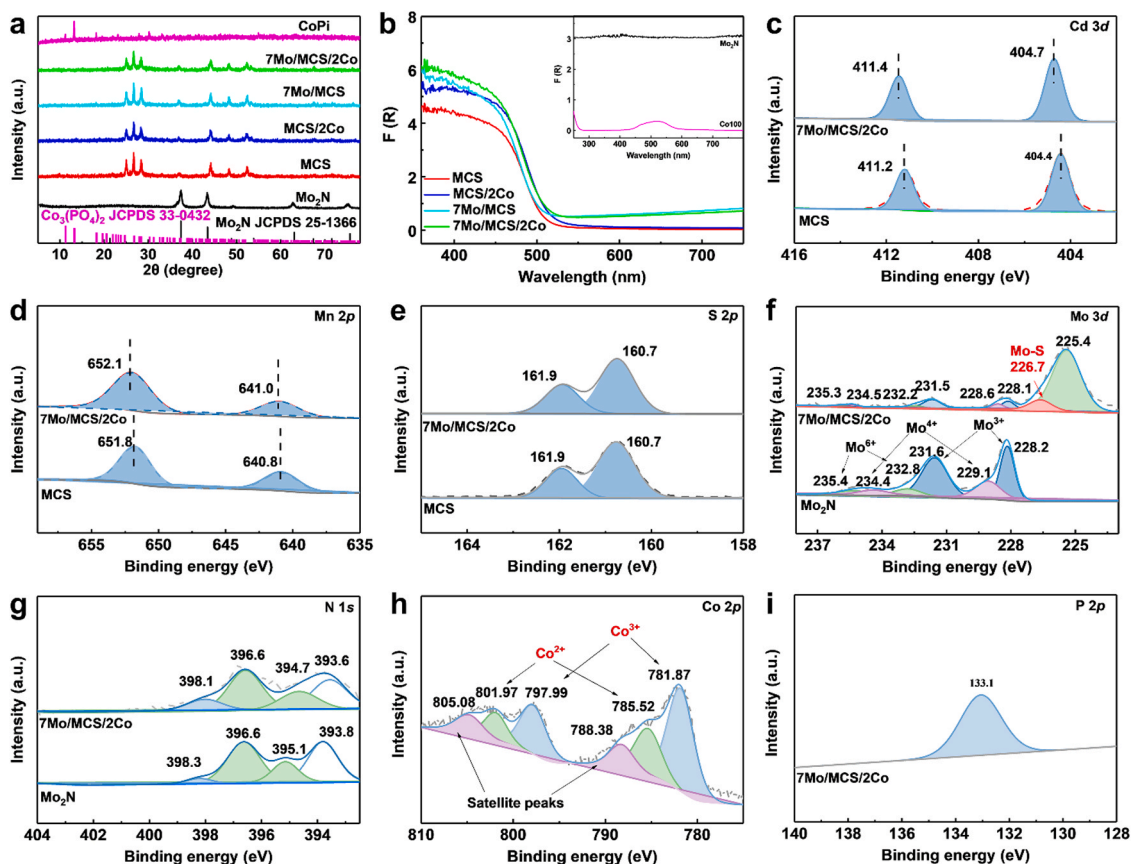


Fig. 2. XRD patterns (a) and UV-vis DRS (b) of Mo<sub>2</sub>N, CoPi, MCS, 7Mo/MCS, MCS/2Co and 7Mo/MCS/2Co samples. The high resolution XPS spectra of (c) Cd 3d, (d) Mn 2p, (e) S 2p, (f) Mo 3d, (g) N 1s, (h) Co 2p, (i) P 2p of the samples.

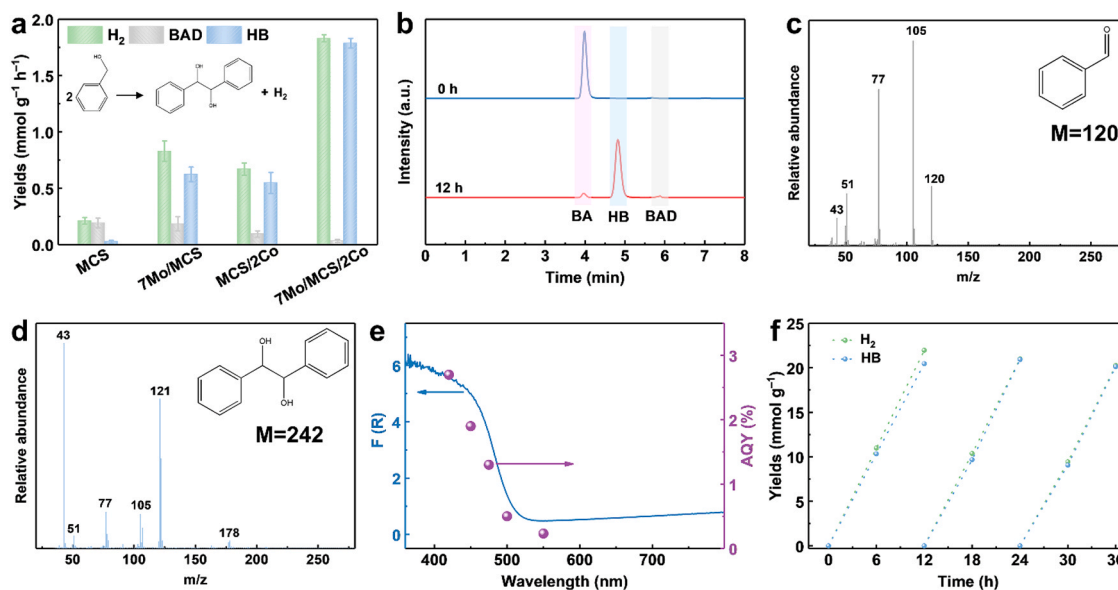


Fig. 3. (a) Activity of photocatalytic H<sub>2</sub> production pairing with HB synthesis of the as-prepared samples, (b) High performance liquid chromatography (HPLC) analysis chromatogram of benzyl alcohol (BA), benzaldehyde (BAD) and hydrobenzoin (HB), Mass spectra of the obtain liquid-products of (c) BAD and (d) HB. (e) DRS spectrum of 7Mo/MCS/2Co composite (left axis) and AQY of HB from C–C coupling of BA versus the incident light wavelength (right axis), (f) Recycling experiments of the 7Mo/MCS/2Co samples.

the introduction of Mo<sub>2</sub>N and CoPi onto MCS can not only improve the H<sub>2</sub>-generation rate, but also tune the selectivity for BA oxidation (Fig. S6). The as-prepared 7Mo/MCS/2Co shows an optimum performance among the investigated samples (Fig. 3a). The average H<sub>2</sub>-

generation rate of 1.83 mmol g<sup>-1</sup> h<sup>-1</sup> was obtained after 12 h irradiation, which is around 8.71, 2.20 and 2.73 times than that of blank MCS, single cocatalyst loading MCS/2Co and 7Mo/MCS, respectively. Meanwhile, the conversion of BA improves from 6.05% to 35.78%, 29.68%

and 90.20%. Specifically, over 7Mo/MCS/2Co, a HB production rate of  $1.79 \text{ mmol g}^{-1} \text{ h}^{-1}$  can be obtained with a yield of 89.45% (12 h reaction time) and a high selectivity of above 98.24% (Fig. 3b-d). The wavelength-dependent HB produced from C–C coupling and AQE measurement of 7Mo/MCS/2Co composite have been performed. The apparent quantum yield (AQY) for the 7Mo/MCS/2Co composite, calculated as the number of charge carriers (holes) used for the HB production divided by the number of incident photons, depends strongly on the light wavelength and well matches the DRS spectrum for the 7Mo/MCS/2Co composite, as shown in Fig. 3e. The corresponding AQE at 420 nm reached 2.71%, which is significantly higher than that of the MCS NRs, 7Mo/MCS and MCS/2Co composite. Moreover, as shown in Supplementary Table S4, it can be found that the photocatalytic activity and selectivity of 7Mo/MCS/2Co composite in BA conversion has exceeded that of most recently reported catalysts. The efficacy of the 7Mo/MCS/2Co composite was also tested for recyclability of three successive runs. No obvious loss of the activity is observed after 3 cycles over a total reaction time of 36 h (Fig. 3f), suggesting its high stability during photocatalytic  $\text{H}_2$  evolution and C–C coupling organic synthesis process. The used 7Mo/MCS/2Co sample was further examined by XRD and XPS, and the unchanged XRD pattern and XPS spectrum of the composite are observed (Fig. S7). The results indicate that the 7Mo/MCS/2Co photocatalyst possesses good structural stability in the photocatalytic system.

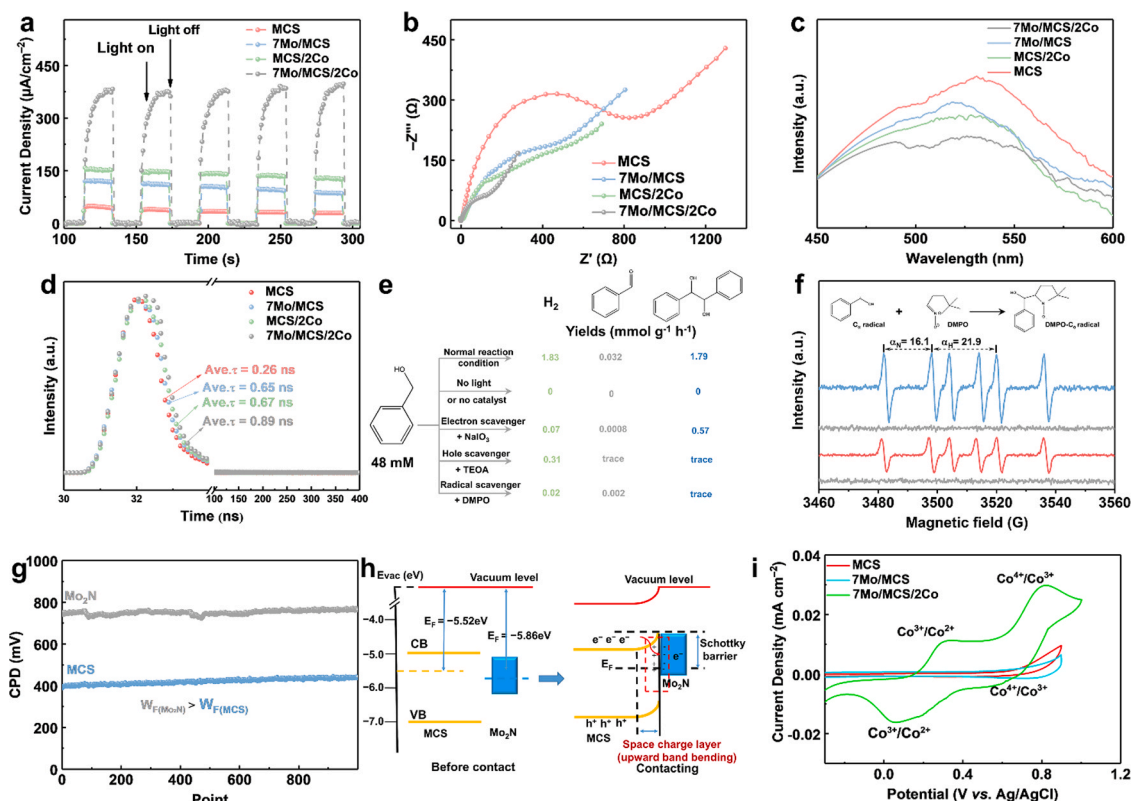
### 3.4. Discussion of the photocatalytic mechanism

Photocurrent responses and electrochemical impedance spectra (EIS) were carried out over MCS, 7Mo/MCS, MCS/2Co and 7Mo/MCS/2Co. As shown in Fig. 4a, MCS NRs show the lowest photocurrent density,

while the introduction of  $\text{Mo}_2\text{N}$  or CoPi obviously raises the current density. In particular, when CoPi and  $\text{Mo}_2\text{N}$  are loaded onto MCS NRs simultaneously, the 7Mo/MCS/2Co composite shows the highest photocurrent density. The EIS of 7Mo/MCS/2Co shows the smallest semicircles among the four investigated samples (Fig. 4b), suggesting a most effective electron-hole pairs separation and transport over 7Mo/MCS/2Co. PL spectra and time-resolved photoluminescence spectra (TRPL) have also been performed. As shown in Fig. 4c, the PL emission intensity decreases in the following order: 7Mo/MCS/2Co < MCS/2Co < 7Mo/MCS < bare MCS. And the TRPL spectra (Fig. 4d and Table S3) show that 7Mo/MCS/2Co has the longest charge carrier lifetime among the four samples, indicating that charge recombination can be better suppressed after loading  $\text{Mo}_2\text{N}$  and CoPi.

To reveal the reaction mechanism of HB formation in the photo-redox catalytic system, we conducted a series of control experiments, as disclosed in Fig. 4e. Removing the catalyst or light irradiation, no product was detected, indicating that the reaction is a photocatalytic process. The introduction of a hole scavenger (TEOA) into the system retarded the HB and BAD formation, whereas the formation of  $\text{H}_2$  ceased after the addition of an electron scavenger ( $\text{NaIO}_3$ ), showing that both photogenerated electrons and holes participate in the formation of  $\text{H}_2$ , BAD and HB on the 7Mo/MCS/2Co photocatalyst. In addition, BAD is always kept at a very low concentration during the reaction (Fig. S8), the production rate of HB matches the production rate of  $\text{H}_2$  very well, indicating the BAD is not an intermediate product but a by-product [16]. Furthermore, it is noted that the addition of the radical scavenger 5, 5-dimethyl-1-pyrroline-N-oxide (DMPO) also significantly inhibited the production of HB (Fig. 4e), indicating that the formation of HB is through radicals intermediates [29].

To gain more hints on radical intermediates mechanism, the electron



**Fig. 4.** (a) Transient photocurrent responses, (b) Nyquist impedance plots, (c) Steady-state photoluminescence spectra, (d) Time-resolved photoluminescence spectra decay of MCS, 7Mo/MCS, MCS/2Co and 7Mo/MCS/2Co. (e) Control experiments with different additives catalyzed by 7Mo/MCS/2Co composites. Scavenger concentrations: 24 mM  $\text{NaIO}_3$ , 24 mM triethanolamine (TEOA), and 24 mM DMPO. Reaction time: 12 h. (f) In situ EPR spectra of MCS and 7Mo/MCS/2Co composites in argon (Ar)-saturated  $\text{CH}_3\text{CN}$  solution in the presence of DMPO. (g) Contact potential difference (CPD) of the MCS and  $\text{Mo}_2\text{N}$ , (h) The Schottky contact between  $\text{Mo}_2\text{N}$  and MCS. (i) Cyclic voltammetry (CV) curves of samples.

paramagnetic resonance (EPR) technique using DMPO as a spin-trapping reagent is utilized to detect the carbon-centered free radicals in this reaction. Fig. 4f shows six characteristic signal peaks belonging to the DMPO- $C_{\alpha}$  radical adduct under light irradiation for both MCS and the 7Mo/MCS/2Co composite, indicating the existence of carbon-centered radical intermediate in this photocatalytic system. [30] Furthermore, a quantitative analysis has been performed to measure the hydrogen and nitrogen hyperfine plittings ( $\alpha_H$ ,  $\alpha_N$ ) for the nitroxide nitrogen. The result suggests  $\alpha_H = 21.9$  and  $\alpha_N = 16.1$ , which are similar to the reported values for DMPO-CH(OH)Ph in the previous literature [14]. In addition, the signal intensities of DMPO-CH(OH)Ph radicals over the 7Mo/MCS/2Co composites are stronger than that for MCS, indicating that a larger amount of such  $\bullet$ CH(OH)Ph radicals can be photogenerated in a 7Mo/MCS/2Co-catalyzed system, which is consistent with the photoactivity trend. Consequently, the 7Mo/MCS/2Co photocatalyst markedly favors the C–C coupling of as-obtained  $\bullet$ CH(OH)Ph radicals.

The work function (WF) of MCS and Mo<sub>2</sub>N were measured by Kelvin probe. As demonstrated in Fig. 4g, the average contact potential difference (CPD) of Mo<sub>2</sub>N and MCS are 760 and 420 mV, respectively. Accordingly, the WF of Mo<sub>2</sub>N and MCS are calculated to be 5.86 and 5.52 eV, respectively, which indicates that the Fermi level of Mo<sub>2</sub>N is

more negative than that of MCS (Fig. 4h). The formation of the Schottky junction at the interface of MCS and Mo<sub>2</sub>N makes the electrons transfer from MCS to Mo<sub>2</sub>N until equilibrium is reached. And a built-in electric field, with positively charged MCS and negatively charged Mo<sub>2</sub>N, is thus formed.

The value of standard potentials of  $E(\text{Co}^{3+}/\text{Co}^{2+})$  and  $E(\text{O}_2/\text{H}_2\text{O})$  are +1.74 and +1.23 V (vs NHE), respectively, indicating that it is thermodynamically favorable for the photogenerated holes to oxidize  $\text{Co}^{2+}$  of CoPi to  $\text{Co}^{3+}$ , and  $\text{Co}^{3+}$  then oxidizes water to oxygen and returns to  $\text{Co}^{2+}$  [31,32]. It was further supported by the cyclic voltammetry (CV). The CV of 7Mo/MCS/2Co shows two pairs of reversible redox peaks (Fig. 4i), which are assigned to the redox couple of  $\text{Co}^{3+}/\text{Co}^{2+}$  and  $\text{Co}^{4+}/\text{Co}^{3+}$ , respectively [33,34]. In contrast, no redox peaks are observed for MCS and 7Mo/MCS.

To verify the photogenerated charge transfer route, the photo-deposition of 7Mo/MCS/2Co with Pt or PbO<sub>2</sub> probe was carried out. As shown in Fig. 5a, b, Pt particles are clearly deposited on Mo<sub>2</sub>N, while no Pt are observed on MCS or CoPi (Fig. S10), implying that the photogenerated electrons in the 7Mo/MCS/2Co sample transfer from MCS to Mo<sub>2</sub>N [9]. As shown in Fig. 5c, d, PbO<sub>2</sub> particles deposited on CoPi, while there are no lattice fringes of PbO<sub>2</sub> on MCS or Mo<sub>2</sub>N (Fig. S11),

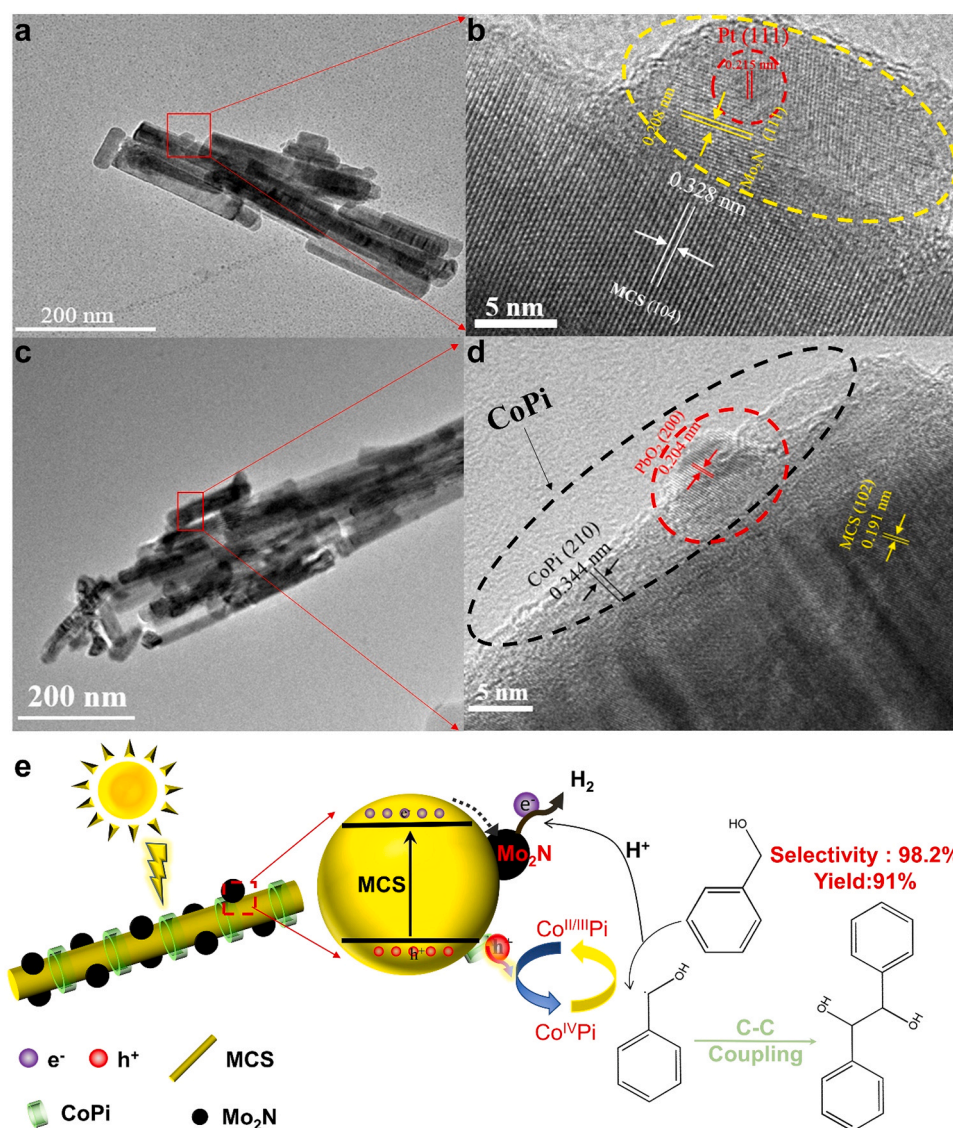


Fig. 5. (a, b) TEM images of 7Mo/MCS/2Co photocatalyst with Pt, (c, d) TEM images of 7Mo/MCS/2Co photocatalyst with PbO<sub>2</sub>. (e) Possible mechanism for the photocatalytic hydrogen evolution of the Mo/MCS/Co samples.



implying that the photogenerated holes of MCS NRs transfer to CoPi [35]. These results convincingly verify that Mo<sub>2</sub>N mainly serves as active sites of reduction while CoPi serves as the oxidation sites.

Based on the results presented above, a mechanism for photocatalytic hydrogen production by water spitting over the Mo/MCS/Co composites is proposed in Fig. 5e. Under irradiation, the photoexcited electrons on the VB of MCS NRs are excited to the CB, then transferred to Mo<sub>2</sub>N through a interfacial Mo-S bond, and the protons denoted by BA are reduced to H<sub>2</sub>. In the meantime, the photoexcited holes on the VB of MCS NRs migrate to CoPi and the Co<sup>2+/3+</sup> of CoPi is oxidized to Co<sup>4+</sup>. Then Co<sup>4+</sup> first oxidize the C-H bond of BA, affording •CH(OH)Ph radicals and returns to Co<sup>2+/3+</sup>, which promotes the separation of photogenerated holes through the cycle of Co<sup>2+/3+</sup> → Co<sup>4+</sup> → Co<sup>2+/3+</sup>. Then, the •CH(OH)Ph radicals can either be further oxidized by holes to generate BAD or combine with another •CH(OH)Ph radical to form HB. Therefore, there is a mutual promotion between the CoPi-mediated hole transfer and the Mo<sub>2</sub>N-mediated electron transfer, greatly improving the charge separation efficiency, leading to an enhanced photoactivity and selectivity of C-C coupling products compared with MCS.

#### 4. Conclusions

In conclusion, a Mo<sub>2</sub>N/Mn<sub>0.3</sub>Cd<sub>0.7</sub>S/CoPi composite with spatial separation of oxidation and reduction sites was fabricated by electrostatic self-assembly and photodeposition method. The Mo<sub>2</sub>N/Mn<sub>0.3</sub>Cd<sub>0.7</sub>S/CoPi composite exhibits remarkably enhanced photocatalytic activities and selectivity of C-C coupling products than that Mn<sub>0.3</sub>Cd<sub>0.7</sub>S loaded with single cocatalyst. The excellent photocatalytic activity of Mo<sub>2</sub>N/Mn<sub>0.3</sub>Cd<sub>0.7</sub>S/CoPi composite can be attributed to the synergetic effect of the Mo<sub>2</sub>N and CoPi dual cocatalysts. In particular, the cage-like hole cocatalyst CoPi can be used as the C<sub>α</sub> radical intermediates recognition active site to control the adsorption-desorption behavior of the substrate molecule and enhance its interaction with the photocatalyst, thereby exhibiting a superior selectivity of C-C coupling products. The interfacial Mo-S bond formed between Mo<sub>2</sub>N and MCS creates direct electron transfer channels and further improves the photocatalytic activity. This work provides a promising route to engineer efficient synergistic dual cocatalysts modified photocatalysts for visible-light-driven cooperative photoredox-catalyzed production of solar fuels and selective organic synthesis of value-added chemical feedstocks. Moreover, to advance the practical applications of such a dual-functional photocatalytic system, besides the rational design and synthesis of highly efficient photocatalysts, it is also an important direction to rationally design continuous flow photoreactor, which can not only increase the interfacial interaction between catalysts and organic substrates induced by the enhanced mass-transfer abilities, but also separate the reactants and target products in time.

#### CRedit authorship contribution statement

**Jing Wang:** Conceptualization, Methodology, Resources, Investigation, Writing – original draft. **Mingyu Qi:** Formal analysis. **Xuxu Wang:** Funding acquisition. **Wenyue Su:** Supervision, Writing – review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2021.120812.

#### References

- [1] W. Che, W. Cheng, T. Yao, F. Tang, W. Liu, H. Su, Y. Huang, Q. Liu, J. Liu, F. Hu, Z. Pan, Z. Sun, S. Wei, Fast photoelectron transfer in (Cring)-C<sub>3</sub>N<sub>4</sub> plane heterostructural nanosheets for overall water splitting, *J. Am. Chem. Soc.* 139 (2017) 3021–3026.
- [2] Z. Xiong, L. Huang, J. Peng, Y. Hou, Z. Ding, S. Wang, Spinel-type mixed metal sulfide NiCo<sub>2</sub>S<sub>4</sub> for efficient photocatalytic reduction of CO<sub>2</sub> with visible light, *ChemCatChem* 11 (2019) 5513–5518.
- [3] M.Y. Qi, Y.H. Li, F. Zhang, Z.R. Tang, Y. Xiong, Y.-J. Xu, Switching light for site-directed spatial loading of cocatalysts onto heterojunction photocatalysts with boosted redox catalysis, *ACS Catal.* 10 (2020) 3194–3202.
- [4] M.Y. Qi, M. Conte, M. Anpo, Z.R. Tang, Y.J. Xu, Cooperative coupling of oxidative organic synthesis and hydrogen production over semiconductor-based photocatalysts, *Chem. Rev.* (2021), <https://doi.org/10.1021/acs.chemrev.1c00197>.
- [5] N. Zhang, M.Y. Qi, L. Yuan, X. Fu, Z.R. Tang, J. Gong, Y.J. Xu, Broadband light harvesting and unidirectional electron flow for efficient electron accumulation for hydrogen generation, *Angew. Chem. Int. Ed.* 58 (2019) 10003–10007.
- [6] S. Xu, M.H. Huang, T. Li, Z.Q. Wei, X. Lin, X.C. Dai, S. Hou, X.Y. Fu, F.X. Xiao, Modulating charge migration in photoredox organic transformation via exquisite interface engineering, *J. Mater. Chem. A* 8 (2020) 8360–8375.
- [7] S. Xu, H.J. Lin, X. Lin, X.Y. Fu, S. Hou, Z.Q. Wei, Q.L. Mo, F.X. Xiao, Intercalating ultrathin polymer interlayer for charge transfer cascade towards solar-powered selective organic transformation, *J. Catal.* 399 (2021) 150–161.
- [8] Z.Q. Wei, S. Hou, X. Lin, S. Xu, X.C. Dai, Y.H. Li, J.Y. Li, F.X. Xiao, Y.J. Xu, Unexpected boosted solar water oxidation by nonconjugated polymer-mediated tandem charge transfer, *J. Am. Chem. Soc.* 142 (2020) 21899–21912.
- [9] J. Wang, Y. Zhang, X. Wang, W. Su, Simultaneous enhancements in photoactivity and anti-photocorrosion of Z-scheme Mn<sub>0.25</sub>Cd<sub>0.75</sub>S/WO<sub>3</sub> for solar water splitting, *Appl. Catal. B: Environ.* 268 (2020), 118444.
- [10] S. Wang, B.Y. Guan, X. Wang, X.W.D. Lou, Formation of hierarchical Co<sub>9</sub>S<sub>8</sub>@ZnIn<sub>2</sub>S<sub>4</sub> heterostructured cages as an efficient photocatalyst for hydrogen evolution, *J. Am. Chem. Soc.* 140 (2018) 15145–15148.
- [11] H.K. Wu, Y.-H. Li, M.Y. Qi, Q. Lin, Y.J. Xu, Enhanced photocatalytic CO<sub>2</sub> reduction with suppressing H<sub>2</sub> evolution via Pt cocatalyst and surface SiO<sub>2</sub> coating, *Appl. Catal. B: Environ.* 278 (2020), 119267.
- [12] Y. Qin, M. Hao, C. Xu, Z. Li, Visible light initiated oxidative coupling of alcohols and o-phenylenediamines to synthesize benzimidazoles over MIL-101(Fe) promoted by plasmonic Au, *Green. Chem.* 23 (2021) 4161–4169.
- [13] Q. Lin, Y.H. Li, M.Y. Qi, J.Y. Li, Z.R. Tang, M. Anpo, Y.M.A. Yamada, Y.J. Xu, Photoredox dual reaction for selective alcohol oxidation and hydrogen evolution over nickel surface-modified ZnIn<sub>2</sub>S<sub>4</sub>, *Appl. Catal. B: Environ.* 271 (2020), 118946.
- [14] M.Y. Qi, Y.H. Li, M. Anpo, Z.R. Tang, Y.J. Xu, Efficient photoredox-mediated C-C coupling organic synthesis and hydrogen production over engineered semiconductor quantum dots, *ACS Catal.* 10 (2020) 14327–14335.
- [15] L. Yuan, M.Y. Qi, Z.R. Tang, Y.J. Xu, Coupling strategy for CO<sub>2</sub> valorization integrated with organic synthesis by heterogeneous photocatalysis, *Angew. Chem. Int. Ed.* 60 (2021) 2–25.
- [16] Q. Guo, F. Liang, X.B. Li, Y.J. Gao, M.Y. Huang, Y. Wang, S.G. Xia, X.Y. Gao, Q. C. Gan, Z.S. Lin, C.H. Tung, L.Z. Wu, Efficient and selective CO<sub>2</sub> reduction integrated with organic synthesis by solar energy, *Chem* 5 (2019) 2605–2616.
- [17] L. Yuan, Y.H. Li, Z.R. Tang, J. Gong, Y.J. Xu, Defect-promoted visible light-driven C-C coupling reactions pairing with CO<sub>2</sub> reduction, *J. Catal.* 390 (2020) 244–250.
- [18] K.P. McClelland, E.A. Weiss, Selective photocatalytic oxidation of benzyl alcohol to benzaldehyde or C-C coupled products by visible-light-absorbing quantum dots, *ACS Appl. Energy Mater.* 2 (2018) 92–96.
- [19] N. Luo, T. Hou, S. Liu, B. Zeng, J. Lu, J. Zhang, H. Li, F. Wang, Photocatalytic coproduction of deoxybenzoin and H<sub>2</sub> through tandem redox reactions, *ACS Catal.* 10 (2019) 762–769.
- [20] X. Sun, D. Jiang, L. Zhang, W. Wang, Alkaline modified g-C<sub>3</sub>N<sub>4</sub> photocatalyst for high selective oxide coupling of benzyl alcohol to benzoin, *Appl. Catal. B: Environ.* 220 (2018) 553–560.
- [21] C. Jiang, H. Wang, Y. Wang, H. Ji, All solid-state Z-scheme CeO<sub>2</sub>/ZnIn<sub>2</sub>S<sub>4</sub> hybrid for the photocatalytic selective oxidation of aromatic alcohols coupled with hydrogen evolution, *Appl. Catal. B: Environ.* 277 (2020), 119235.
- [22] K.Q. Lu, M.Y. Qi, Z.R. Tang, Y.J. Xu, Earth-abundant MoS<sub>2</sub> and cobalt phosphate dual cocatalysts on 1D CdS nanowires for boosting photocatalytic hydrogen production, *Langmuir* 35 (2019) 11056–11065.
- [23] T. Di, B. Zhu, J. Zhang, B. Cheng, J. Yu, Enhanced photocatalytic H<sub>2</sub> production on CdS nanorod using cobalt-phosphate as oxidation cocatalyst, *Appl. Surf. Sci.* 389 (2016) 775–782.
- [24] L. Ge, C. Han, X. Xiao, L. Guo, In situ synthesis of cobalt-phosphate (Co-Pi) modified g-C<sub>3</sub>N<sub>4</sub> photocatalysts with enhanced photocatalytic activities, *Appl. Catal. B: Environ.* 142–143 (2013) 414–422.

- [25] J. Xie, S. Li, X. Zhang, J. Zhang, R. Wang, H. Zhang, B. Pan, Y. Xie, Atomically-thin molybdenum nitride nanosheets with exposed active surface sites for efficient hydrogen evolution, *Chem. Sci.* 5 (2014) 4615–4620.
- [26] X. Wang, X. Wang, J. Huang, S. Li, A. Meng, Z. Li, Interfacial chemical bond and internal electric field modulated Z-scheme  $S_v\text{-ZnIn}_2\text{S}_4/\text{MoSe}_2$  photocatalyst for efficient hydrogen evolution, *Nat. Commun.* 12 (2021) 4112.
- [27] S. Gong, Z. Jiang, P. Shi, J. Fan, Q. Xu, Y. Min, Noble-metal-free heterostructure for efficient hydrogen evolution in visible region: Molybdenum nitride/ultrathin graphitic carbon nitride, *Appl. Catal. B: Environ.* 238 (2018) 318–327.
- [28] M. Barroso, A.J. Cowan, S.R. Pendlebury, M. Gratzel, D.R. Klug, J.R. Durrant, The role of cobalt phosphate in enhancing the photocatalytic activity of  $\alpha\text{-Fe}_2\text{O}_3$  toward water oxidation, *J. Am. Chem. Soc.* 133 (2011) 14868–14871.
- [29] S. Xie, Z. Shen, J. Deng, P. Guo, Q. Zhang, H. Zhang, C. Ma, Z. Jiang, J. Cheng, D. Deng, Y. Wang, Visible light-driven C–H activation and C–C coupling of methanol into ethylene glycol, *Nat. Commun.* 9 (2018) 1181.
- [30] X. Wu, S. Xie, C. Liu, C. Zhou, J. Lin, J. Kang, Q. Zhang, Z. Wang, Y. Wang, Ligand-controlled photocatalysis of CdS quantum dots for lignin valorization under visible light, *ACS Catal.* 9 (2019) 8443–8451.
- [31] B. Pan, Y. Zhou, W. Su, X. Wang, Enhanced photocatalytic  $\text{CO}_2$  conversion over  $\text{LaPO}_4$  by introduction of  $\text{CoCl}_2$  as a hole mediator, *RSC Adv.* 6 (2016) 34744–34747.
- [32] G.H. Moon, M. Yu, C.K. Chan, H. Tuysuz, Highly active cobalt-based electrocatalysts with facile incorporation of dopants for the oxygen evolution reaction, *Angew. Chem. Int. Ed.* 58 (2019) 3491–3495.
- [33] Y. Sasaki, H. Kato, A. Kudo,  $[\text{Co}(\text{bpy})_3]^{(3+/2+)}$  and  $[\text{Co}(\text{phen})_3]^{(3+/2+)}$  electron mediators for overall water splitting under sunlight irradiation using Z-scheme photocatalyst system, *J. Am. Chem. Soc.* 135 (2013) 5441–5449.
- [34] C. Lee, K. Shin, C. Jung, P.P. Choi, G. Henkelman, H.M. Lee, Atomically embedded Ag via electrodiffusion boosts oxygen evolution of  $\text{CoOOH}$  nanosheet arrays, *ACS Catal.* (2019) 562–569.
- [35] W. Jiang, X. Zong, L. An, S. Hua, X. Miao, S. Luan, Y. Wen, F.F. Tao, Z. Sun, Consciously constructing heterojunction or direct Z-scheme photocatalysts by regulating electron flow direction, *ACS Catal.* 8 (2018) 2209–2217.